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Relation between toughness and molecular coupling at cross-linked polymer/solid interfaces

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RELATION BETWEEN TOUGHNESS AND MOLECULAR COUPLING AT CROSS-LINKED POLYMER/SOLID INTERFACES

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CERTIFICATION

I, Michaela Tymichova, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Michaela Tymichova

19 August 2005

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Abstract

The relationship between the interfacial fracture toughness (G_c) and molecular coupling between epoxy polymers and silicon wafers was studied using the asymmetric double cantilever test (ADCT). In order to investigate the molecular coupling, the coupling molecules had to be applied along the polymer/substrate interface in various concentrations. The *grafting from* technique by means of the "living" free radical polymerisation techniques, namely nitroxy-mediated "living" free polymerisation (NMP) and atom transfer radical polymerisation (ATRP), were used to prepare suitable coupling molecules. Unfortunately, these techniques did not produce satisfactory results, and the new route of *grafting to* was investigated. This method involved chemical attachment of brominated polystyrene chains (PS) to the silicon substrate. The bromine functional groups of the brominated polystyrene (PS(Br)) were then further converted to amino ($-NH_2$) groups using the Heck reaction, producing PS(NH_2).

The conversion method was first tested using the free (unattached) polystyrene (MW = 200K) which was brominated (molar fraction of brominated units, x = 0.1). The conversion from PS to PS(Br) and then to PS(NH_2) was monitored by proton and carbon nuclear magnetic resonance techniques (^{1}H-NMR and ^{13}C-NMR) and gel permeation chromatography.

For the *grafting to* experiments, monochlorosilane end-functionalised polystyrene (PS-$SiClMe_2$) (MW = 8000) was used. Various ratios of PS and PS(Br) ranging from 0 to 20% PS(Br) were deposited onto silicon substrates. Applying the Heck reaction, Br groups were converted to NH_2, producing surfaces with different concentrations of amino groups which were expected to react with the epoxy polymer.

ADCT was adapted to investigate the dependence of the interfacial fracture toughness on the degree of coupling. The dependence of G_c on the concentration of the coupling molecules was not directly confirmed. This was attributed mainly to the

challenges in deposition of the polymer chains and the final conversion to PS(NH_2). However, the differences in G_c values between experiments suggested that G_c's measured by ADCT reflect the differences in surface properties of the polymer modified surfaces, and therefore this technique is suitable for interfacial adhesion measurements between epoxy polymers and solid substrate.

I dedicate this thesis to all people who dare to be different, to all who yearn for achieving something that seems impossible but they do it anyway. Sometimes, the results are not what we expected or were hoping for. It does not matter. The important thing is that the seeds were planted.

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